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(54) Title: WATERBORNE DISPERSIONS OF POLYURETHANE AND ETHYLENIC POLYMERS (57) Abstract Homogeneous dispersions of polyurethane and polyethylenic polymers are made by dispersing an isocyanate prepolymer into an aqueous dispersion of the polyethylenic polymer, and then chain extending the prepolymer. The resulting dispersion exhibits a single glass transition temperature.		

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WATERBORNE DISPERSIONS OF POLYURETHANE
AND ETHYLENIC POLYMERS

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The present invention relates to aqueous dispersions containing both polyurethane polymers, and ethylenic polymers.

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Polyurethanes find use in a variety of applications, including coatings, paints, adhesives, and the manufacture of fibers and solid articles.

10

Polyurethanes are typically soluble in organic solvents, and exhibit little if any solubility in aqueous solvents or in systems in which water and a second water-soluble solvent are employed. Organic solvent-based resin solutions have thus typically been the vehicle of choice for use in forming coatings and the like of polyurethanes. However, many organic

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solvents commonly used in conjunction with such resins present environmental problems associated with their toxicity. There has been a growing concern based on the effects of such organic solvents on the environment, as well as on the long-term health of

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individuals who come into contact with such solvents. There has, therefore, been a growing interest in the use of aqueous resin compositions as a means of

eliminating toxicity problems associated with organic solvents, and as a means of complying with

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governmental edicts with respect to the use of such solvents.

For many applications, it would be desirable to incorporate several types of polymer into a given dispersion, to obtain the benefits of each polymer's

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desirable properties. Doing so is not at all

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straightforward, because of incompatibilities between
1 the polymers and/or the vehicles in which they are
solubilized or dispersed.

Various processes have been proposed for
forming dispersions of polyurethane and acrylates or
5 other ethylenic polymers. These however do not
uniformly provide satisfactory approaches.

U.S. Patent No. 4,318,833 discloses that a
urethane/acrylic dispersion could be made by adding an
ethylenic monomer to a fully reacted polyurethane
10 dispersion and then polymerizing the monomer by free
radical initiation.

U.S. Patents No. 4,644,030 and No. 5,169,895
describe a process in which a urethane prepolymer is
prepared as a solution in an ethylenic monomer. This
15 mixture is dispersed in water, the prepolymer is chain
extended and the monomer is then polymerized by free
radical initiation.

European Patent Application No. 0 510 572 A2
discloses the preparation of urethane/vinyl polymer
20 dispersions by the addition of ethylenic monomers to a
completely reacted urethane prepolymer to give a
solution which is dispersed in water. The monomer is
then polymerized by free radical initiation and the
prepolymer is chain extended.

25 The present invention is thus directed to an
improved technique for forming aqueous dispersions
containing both polyurethane, which technique affords
improved ease of operation, more satisfactory yields,
and offers a greater variety in the selection of

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reactants and in the range of properties of the
1 products that can be obtained.

More specifically, the present invention is
directed to a process for producing an aqueous
dispersion of polyurethane and polyethylenic polymers,
5 comprising

(a) providing a urethane prepolymer
substituted with an average of at least 2 isocyanate
groups, per molecule;

(b) providing an aqueous dispersion of a
10 polyethylenic polymer;

(c) combining said prepolymer and said
aqueous dispersion to form a combined dispersion which
is homogeneous; and

(d) chain extending said prepolymer in said
15 combined dispersion.

The present invention also includes the
stable aqueous dispersions resulting from the
foregoing method of this invention, the use of such
dispersions for application in a film-forming amount
20 to a substrate with subsequent drying thereon, and the
resulting dried, cured and hardened films which may be
permanently coated on the substrate or made self-
supporting involving use of a substrate with a release
surface. The dispersions of the invention may also be
25 used in the above manner or otherwise as impregnants
and sizing for paper, textiles and other foraminous
materials, as pigment binders and adhesives, and for
making cross-linked brittle polymeric products when
the dispersion contains non-elastomeric, non-film
30 polyurethanes.

The method of this invention yields several
1 unexpected improvements relative to the method
disclosed in U.S. Patent No. 4,318,833 which produces
a different type of aqueous dispersion containing
polyurethanes and polymerized ethylenically
5 unsaturated monomers. The necessity of using an
organic solvent medium (with its attendant
disadvantages) in the reaction for producing the fully
chain-extended polyurethane is eliminated. The
ethylenic polymer becomes intimately, homogeneously
10 and/or molecularly intermixed with the polyurethane
prepolymer in the reaction medium, so the subsequent
chain extension of the prepolymer provides thereby a
true, more thorough in situ dispersion. The resulting
aqueous dispersions of this invention thereby yield
15 films and other products with unexpectedly improved
properties with respect to rapidity of curing and
hardening, resistance to water, organic solvents and
environmental conditions, tensile strength, modulus of
elasticity, and/or elongation and the like.
20 The products formed in accordance exhibit a
single glass transition temperature (T_g). This
characteristic confirms that the products are distinct
from mere mixtures of polyurethanes and polyethylenic
polymers, which would exhibit at least two glass
25 transition temperatures.

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The prepolymer is terminated with preferably
1 an average of at least two isocyanate (-NCO) groups
per molecule.

NCO-terminated polyurethane prepolymers,
preferably employed herein, are commonly produced by
5 reacting organic material containing an average of at
least about 2 active hydrogen atoms per molecule,
usually a diol and preferably a polyester polyol,
with a stoichiometric excess of an organic
diisocyanate, preferably methylene bis (isocyanato
10 cyclohexane). Preferably a suitable proportion of the
said organic material also contains anionic
substituent groups for providing water dispersibility
to the prepolymer, such as at least one comparatively
unreactive pendant carboxylic or sulfonate group, in
15 salt form or preferably neutralized with a suitable
basic material to salt form during or after the
prepolymer formation or during the formation of the
dispersion. Any organic polyisocyanates may be used
in the process according to the invention. It is
20 preferred to use polyisocyanates of the formula
 $Q(NCO)_2$, wherein Q represents an aliphatic hydrocarbon
group containing from 4 to 12 carbon atoms, a
cycloaliphatic hydrocarbon group containing from 6 to
15 carbon atoms, an aromatic hydrocarbon group
25 containing from 6 to 15 carbon atoms or an araliphatic
hydrocarbon group containing from 7 to 15 carbon
atoms. The most preferred diisocyanate is isophorone
diisocyanate. The following are examples of other
preferred diisocyanates: tetramethylene-diisocyanate,
30 hexamethylene diisocyanate, dodecamethylene-

- diisocyanate, 1,4-diisocyanato-cyclohexane, 1-
1 isocyanato-3, 3, 5-trimethyl-5-isocyanatomethyl
cyclohexane, 4,4'-diisocyanatodicyclohexylemethane,
4,4'-diisocyanato-dicyclohexyl-propane-(2,2); 1,4-
diisocyanato-benzene, 2,4-diisocyanatotoluene, 2,6-
5 diisocyanatotoluene, 4,4'-diisocyanatodiphenylmethane,
4,4'-diisocyanatodiphenyl-propane-(2,2), p-xylylene-
diisocyanate, a,a,a',a'-tetramethyl-m-or p-xylylene-
diisocyanate and mixtures of these compounds.
Mixtures of any of the foregoing can also be used.
- 10 The mole ratio of diisocyanate to polyol is generally
stoichiometric, e.g. (1.9-2.1):1.

- Reaction of the diisocyanate and the polyol
or polyol polymer can be carried out at moderately
elevated temperatures, e.g. 50°C.-100°C. The reaction
15 is generally carried out in an inert solvent or
without a solvent. One preferred solvent is N-methyl
pyrrolidone. Other suitable solvents include acetone,
methyl ethyl ketone, toluene, dimethyl formamide,
ethyl acetate, tetrahydro furan, and dioxane.

- 20 Suitable polyol reactants preferably have a
molecular weight (M.W.) of about 400 to 5000, and an
average OH value of about 10 to about 1,000,
preferably about 30 to about 150, as determined by
ASTM E222-67, Method B.

- 25 In addition to or instead of the preferred
polyester polyols, other polyols or mixtures thereof
may be employed such as poly-caprolactone,
polycarbonate and polybutadiene resins (hydroxyl
terminated homopolymers of butadiene), polyethers
30 based on ethylene oxide, propylene oxide and

tetrahydrofuran, and the like. Use as reactants of
1 organic material containing an average of more than 2
active hydrogen atoms per molecule, entirely or in
suitable proportions with difunctional reactants,
enable the production (from the aqueous dispersions of
5 this invention) of cross-linked brittle polymeric
products which are commercially useful though neither
elastomeric or film-forming.

Similar considerations apply with respect to
the isocyanate reactant which, in addition to or
10 instead of the preferred organic diisocyanate may
include organic materials containing an average of
more than two isocyanate groups. Examples of suitable
commercially available polyisocyanates include Mondur
CB (adduct of 3 moles toluene diisocyanate with 1 mole
15 trimethylol propane, Bayer), Desmodur-N,
(trifunctional biuret of 1,6-hexane diisocyanate,
Bayer), Isonate 143L (polymeric methylene bis(phenyl
isocyanate), Upjohn) and the like. On the other hand,
monofunctional isocyanate and active hydrogen
20 containing material may also be employed, but in
suitable small proportions, preferably below about 10
wt.% of the prepolymer reactants, since they yield end
caps resulting in chain termination.

The NCO-terminated polyurethane prepolymers
25 employed in this invention are preferably rendered
water dispersible by including in the prepolymer chain
an effective water-dispersing amount of pendant
carboxylic or cationic salt groups such as sulfonate
groups. Such amount is typically about 0.5 to about
30 10 wt.% of such groups. Alternatively, the monomer-

containing prepolymer may be devoid of such groups in
1 which case it is then dispersed in water with the aid
of a dispersing agent, preferably a nonionic
ethoxameric surfactant.

According to an optional feature of this
5 invention, the polyurethane chain in known manner
contains about 1 to about 5 wt.% of units derived from
melamine, thereby providing films produced from the
present aqueous dispersions with improved resistance
to organic solvents.

10 According to another optional feature of
invention, the polyurethane is provided in known
manner with cross-linking, curable, hardening groups
activated to self condensation and cross-linking upon
drying of the film on a substrate under ambient
15 conditions, such groups comprising about 2 to about 10
wt.% of N-methylol hydrazide termini or end caps.

B. THE POLYETHYLENIC POLYMER DISPERSION

20 By "polyethylenic polymer" is meant herein a
polymer obtained by polymerization of monomers having
polymerizable ethylenic (that is, C=C) unsaturation.
Homopolymers are contemplated as are copolymers of two
(or more) different ethylenically unsaturated
25 monomers.

Examples of such monomers include butadiene,
isoprene, styrene, alpha-methyl styrene and the like;
substituted styrenes such as chlorostyrene,
dichlorostyrene, bromostyrene, p-vinylphenyl phenyl
30 oxide and the like; the acrylic and substituted

acrylic monomers such as acrylic acid, methacrylic
1 acid, cyclohexyl acrylate and methacrylate, benzyl
acrylate and methacrylate, the C₁₋₆ alkyl acrylates and
methacrylates such as methyl, ethyl and butyl acrylate
and methacrylate, phenyl acrylate, phenyl
5 methacrylate, alphachloroacrylonitrile and the like;
the vinyl esters and vinyl ethers such as vinyl
acetate, vinyl acrylate, vinyl methacrylate, vinyl
propyl ethers, vinyl butyl ethers and the like; other
water soluble monomers, especially hydroxy -C₁-C₆-
10 alkyl esters such as hydroxy ethyl acrylate or
methacrylate, hydroxy propyl acrylate or methacrylate
and the like. Any of the known polymerizable monomers
can be used and the compounds listed above are
illustrative and not restrictive of the monomers
15 suitable for use in this invention.

The ethylenically unsaturated monomers which
are preferred in the practice of this invention
include the (meth)acrylic and substituted
(meth)acrylic monomers as well as styrene.

20 The aqueous dispersion used in the
present invention is preferably prepared by emulsion
polymerization of the monomers or comonomers in an
aqueous system. The reagents necessary for emulsion
polymerization are those conventionally employed,
25 including a free radical initiator (typically a peroxy
compound) and a surfactant (typically an anionic
surfactant, such as alkyl sulfonates, alkyl aryl
sulfonates, or alkyl aryl polyalkoxy sulfonates). The
conditions for carrying out the emulsion
30 polymerization are likewise those conventionally

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employed, and are familiar to those of ordinary skill
1 in this art.

C. COMBINING THE PREPOLYMERS AND THE AQUEOUS

5 DISPERSION

The polyurethane prepolymer, which is preferably free of ethylenically unsaturated monomeric compounds, is next combined with the aqueous
10 dispersion of the polyethylenic polymer. The ratio by weight of the polyurethane to the polyethylenic polymer should be in the range of 10:90 to 90:10 and more preferably 70:30 to 30:70.

The polyurethane prepolymer and the
15 polyethylenic polymer dispersion are preferably combined by dispersing the polyurethane prepolymer into the dispersion of the polyethylenic polymer. This can be accomplished by providing the polyethylenic polymer dispersion in a vessel and then
20 adding thereto the prepolymer while the vessel contents are being subjected to high shear agitation. The presence of the surfactant(s) used in the emulsion polymerization step assists in formation of a stable aqueous dispersion of the prepolymer and the
25 polyethylenic polymer.

D. CHAIN EXTENDING THE PREPOLYMER

The prepolymer is next reacted with a suitable chain extender, which reacts with the
30 isocyanate groups. Satisfactory chain extenders

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include diamines such as hydrazine, and alkyl and
1 aromatic polyols, especially diols, and alkyl and
aromatic diamines and triamines, wherein the alkyl
compounds contain a table of 2 to 12 carbon atoms or
the aromatic moiety contains 6 to 10 carbon atoms.
5 Other examples of chain extenders include ethylene
diamine, diethylene triamine, 1,2-diaminopropane, 1,3-
diaminopropane, 1,4-diaminobutane, and 3,3,5-
trimethyl-5-aminomethyl cyclohexylamine; and ethylene
glycol, 1,2-dihydroxypropane, 1,6-dihydroxyhexane, and
10 the polyols described herein as useful reactants to
make the polyester.

The product of reaction with the chain
extender is a dispersion of polymeric polyurethane
together with the polyethylenic polymer. This
15 dispersion exhibits functional properties superior to
those exhibited by mixtures obtained by forming the
polyurethane and polyethylenic polymers separately and
then mixing them together.

The aqueous dispersions of this invention
20 are advantageously employed as coating compositions,
for which purpose they may be further diluted with
water and/or organic solvents, or they may be supplied
in more concentrated form by evaporation of water
and/or organic components of the liquid medium. As
25 coating compositions they may be applied to any
substrate including wood, metals, glass, cloth,
plastics, foam and the like, by any conventional
method including brushing, dipping, flow coating,
spraying, and the like. The compositions may contain
30 other conventional ingredients including organic

solvents, pigments, dyes, emulsifiers, surfactants,
1 thickeners, heat stabilizers, leveling agents,
anticratering agents, fillers, sedimentation
inhibitors, UV absorbers, antioxidants and the like
introduced at any stage of the production process or
5 subsequently.

These dispersions are preferably applied to
substrates in effective film-forming amounts depending
on the solids content, temperature and other
conditions, the type of substrate, product desired,
10 etc. The film coating on the substrate may simply be
protective, decorative, and/or intelligence imparting
or the like or serve as an adhesive or other function.
Self-supporting thin or thick films or sheets may be
produced by application to a substrate with a release
15 surface from which the cured, hardened film can be
removed. Hardening and curing on the substrate is
generally accomplished by simply drying under ambient
conditions, which may if desired be expedited and/or
facilitated by concurrent heating, subsequent baking,
20 etc. The dispersions of this invention have good
storage stability and yield films and coatings
with improved properties such as resistance to water,
organic solvents and environmental conditions,
flexibility, elasticity and/or tensile strength, and
25 the like.

The following examples are illustrative of
the present invention and are not intended to limit
its scope.

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EXAMPLE 1

1

Aqueous dispersion of polyurethane (based on neopentyl adipate polyester)/poly(methyl methacrylate-methacrylic acid)

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A. Prepolymer preparation.

A four-necked resin flask equipped with a stirrer, condenser, thermometer and gas inlet tube was
10 charged with 1, 2, 3, 4 and 5 below

1. Neopentyl adipate (OH No.= 112)	365.70 g
2. Dimethylol propionic acid	49.50 g
3. Trimethylol propane	14.50 g
15 4. Methylene bis (isocyanato cyclohexane)	363.00 g
5. N-methyl pyrrolidone	170.00 g
6. Triethylamine	37.30 g

The mixture in the flask was heated under
20 dry air for 4 hours at 80°C-85°C, until the residual isocyanate content was 4.1% (theoretical isocyanate content was 4.1%), then 6. was added and mixed for 30 minutes. The result was a NCO-terminated prepolymer.

25 B. Acrylic dispersion preparation

A four necked flask was equipped with a stirrer, condenser, thermometer and nitrogen inlet tube. A redox initiated polymerization of the methyl
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methacrylate and methacrylic acid monomers was carried
1 out using the following formula -

	1. Deionized Water	1480.00
	2. Triton X-200 (alkyl aryl EO sulfonate)	96.00
5	3. Methyl methacrylate	792.00
	4. Methacrylic acid	8.00
	5. Ferrous sulfate solution	16 mL
	6. Ammonium persulfate	4.00
	7. Sodium metabisulfite (in 20 mL of water)	4.00
10	8. t-Butyl hydroperoxide solution (70%)	20 drops

1 and 2 were added to the flask with
stirring. When the emulsifier had dispersed, 3, 4, 5
and 6 were added and the nitrogen flow was started.
15 The nitrogen was bubbled through the mixture for 15
minutes while stirring and cooling to 20°C, then 7 and
8 were added and the polymerization began after a
short induction period. The exotherm temperature rose
to 60°C in 10 minutes and then fell slowly to 35°C
20 over 40 minutes. At this stage the dispersion was
filtered and had the following properties:

	Total solids content, %	34.2
	Particle charge	anionic
25	Particle size (µm)	0.08
	T _g , °C (calculated)	105.2
	Acid number (calculated)	6.5
	pH (before neutralization with ammonia)	1.9
	pH (after adjustment)	8.1

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C. Urethane/acrylic dispersion preparation.

1

1038 g of deionized water and 1008 g of the poly(methyl methacrylate-methacrylic acid) dispersion from step B were added to a mixing vessel equipped with a high speed stirrer. 1000 g of the NCO-terminated prepolymer from step A, at a temperature of 75°C-80°C, was added to this with vigorous stirring to produce a colloidal dispersion. 40.1 g of 35% hydrazine solution was then added with rapid stirring, to chain extend the NCO- terminated prepolymer. The resulting polyurethane/polymethyl methacrylate dispersion had a pH of 8.25 and a viscosity of 45 cps at 37.5 solids.

15 A film cast from the above dispersion after drying for 1 day at room temperature and then 2 hour at 130°C, had the following tensile properties:

20	Ultimate tensile strength, psi	6325
	Elongation, %	75
	T _g , °C	64

25 As a comparison, a purely physical blend of the polyurethane and the acrylic dispersion was prepared by making a water-borne polyurethane dispersion by the method shown below and blending this with the acrylic dispersion described earlier.

(Comparative) Polyurethane dispersion preparation

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- 1256 g of deionized water was added to a
- 1 mixing vessel equipped with a high speed stirrer.
- 1000 g of the -NCO terminated prepolymer from step A (at a temperature of 75°C-80°C) was added, with vigorous stirring, to produce a colloidal dispersion.
- 5 40.10 g of a 35% hydrazine solution was then added to chain extend the -NCO terminated prepolymer. The resulting polyurethane dispersion had a pH of 8.38 and a viscosity of 35 cps at a TSC of 35%.
- 10 Physical blend of polyurethane dispersion/acrylic dispersion. (70/30 by weight solids)

The dispersions were blended as per the formula

15	Polyurethane dispersion	700.00
	Acrylic dispersion	300.00
	10% Fluorad FC-129 solution	0.70
	Water	80.00
20	Butyl Propasol	40.00
	Dowanol DPM	40.00

- Films were prepared from this blend. These were air-dried overnight and annealed in an oven at
- 25 130°C for 2 hours. The films had the following properties:

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	Tensile strength, psi	5210
1	Elongation, %	50
	T _g , °C	-12,46,117

5 The physical properties of the film prepared from the blended dispersions were inferior to those of the film prepared from urethane/acrylic dispersion of the present invention. The film from the blend also exhibited three T_g values, unlike the dispersion of the present invention; which showed a single T_g. A
10 comparison of the chemical resistance tests carried out on the blend and the dispersion of the present invention also showed the inferiority of the physical blend (see table below):

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Chemical Resistance Tests
(three coats over red oak test pieces)
(0 = best, 5 = worst)

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	PUD/ Acrylic Blend	Urethane/Acrylic Dispersion of the Present Invention
50% ethanol	5	0
Distilled Water	0	0
1N sodium hydroxide	2	0
3% acetic acid	1	0
5% ammonia	1	0
1% Clorox Solution	0	0
2% hydrochloric acid	0	0
Mustard	1	1
409 cleaner	0	0

EXAMPLE 2

20

Aqueous dispersion of polyethylene adipate based polyurethane/poly(methyl methacrylate - methacrylic acid)

A. Prepolymer preparation

25

A 3000 mL resin reactor equipped with a stirrer, heating mantle, thermometer and nitrogen inlet was charged with

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	Polyethylene adipate (M.W. 2000)	1249 g
1	Trimethylol propane	21 g
	Dimethylol propionic acid	124 g
	N-methyl-2-pyrrolidinone	244 g
	Bis-(cyclohexyl) methane diisocyanate	768 g

5

This mixture was stirred and heated to 80°C for 3 hours after which it was cooled to 70°C, and then 94 g of triethylamine was added.

10 B. Acrylic dispersion preparation.

The poly (methyl methacrylate- methacrylic acid) copolymer as described in Example 1, step B, was also used in this example.

15

C. Dispersion Preparation

2517 g of water and 2692 g of the above acrylic dispersion were placed in a mixing vessel and 20 2500 g of the NCO- terminated prepolymer was added to this mixture with high speed stirring. A water temperature of 25° - 35°C was maintained during the addition of the prepolymer. After 5 minutes of high speed mixing 98 g of 35% hydrazine solution was added. 25 This resulted in a 5° - 10°C exotherm.

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The resulting dispersion had the following

1 physical properties:

Total solids content, %	40.7
pH @ 25°C	8.39
5 Viscosity (Brookfield LVF), cps	65

EXAMPLE 3

Aqueous dispersion of poly(ethylene adipate)
10 based urethane with a poly(butyl acrylate-methacrylic acid)

A. Prepolymer preparation

15 The prepolymer was prepared using the same ingredients and same procedure as in Example 2.

B. Acrylic dispersion

20 This was prepared by substituting butyl acrylate for methacrylate in the formula used in Examples 1. and 2.

C. Dispersion preparation

25

The NCO- terminated prepolymer as described in Example 2. was dispersed in 2692 g of the poly(butyl acrylate- methacrylic acid) dispersion and chain extended as in Example 2.

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The physical properties of the resulting dispersion
1 were:

Total solids content, %	40.17
pH @ 25°C	8.17
5 Viscosity (Brookfield LVF, cps)	9

EXAMPLE 4

Aqueous dispersion of a poly(1,6 hexane
10 adipate/isophthalate) based polyurethane/poly(butyl
acrylate-methacrylic acid)

A. Prepolymer preparation

15 A 2000 mL resin reactor equipped with a stirrer,
heating mantle, thermometer and nitrogen inlet was
charged with -

Poly(1,6 hexane adipate/isophthalate)	
20 diol (M.W. 1600)	594.0 g
Dimethyl propionic acid	10.4 g
Bis-(cyclohexyl) methane diisocyanate	189.6 g

and the mixture was stirred and heated to 100°C for
25 three hours. The resulting NCO-terminated prepolymer
had a theoretical % NCO of 2.88.

B. Acrylic dispersion preparation

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The poly(butyl acrylate-methacrylic acid)
1 dispersion prepared as described in Example 3 was
used.

C. Dispersion Preparation

5 The NCO- terminated prepolymer was added,
with high speed stirring, to 1070 g of the poly(butyl
acrylate-methacrylic acid) dispersion containing 7.9 g
of triethylamine and 71 g of a nonionic nonyl phenol
10 surfactant. The dispersion temperature was maintained
below 35°C during the prepolymer addition. After
stirring for 10 minutes, 21.5 g of a 35% solution of
hydrazine was added and an exotherm of 5°-10°C
occurred.

15 The physical properties of the dispersion
were:

	Total solids content, %	60.0
20	pH @ 25°C	7.72
	Viscosity (Brookfield LVF), cps	1100

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WHAT IS CLAIMED IS:

1. A process for producing an aqueous dispersion of polyurethane and polyethylenic polymers, comprising

(a) providing a prepolymer substituted with an average of at least two isocyanate groups per molecule;

(b) providing an aqueous dispersion of a polyethylenic polymer;

(c) dispersing said prepolymer into said aqueous dispersion to form a combined dispersion; and

(d) chain extending said prepolymer in said combined dispersion.

2. A process according to claim 1 wherein said prepolymer is the reaction product of a polyol reactant and a polyisocyanate reactant.

3. A process according to claim 2 wherein said polyol reactant is selected from the group consisting of organic polyols having a molecular weight of 400 to 5,000 and an average OH value of 10 to 1,000.

4. A process according to claim 2 wherein said polyisocyanate reactant has the formula $Q(NCO)_2$, wherein Q is alkyl containing 4 to 12 carbon atoms, cycloalkyl containing 6 to 15 carbon atoms, aromatic containing 6 to 15 carbon atoms, or alkylaromatic containing 7 to 15 carbon atoms.

5. A process according to claim 2 wherein said polyisocyanate reactant is selected from the

group consisting of isophorone diisocyanate and methylene bis(isocyanate cyclohexane).

6. A process according to claim 2 wherein said polyol is selected from the group consisting of dimethylol propionic acid and trimethylol propane.

7. A process according to claim 1 wherein said polyethylenic polymer is a homopolymer or copolymer of monomers selected from the group consisting of acrylic acid, methacrylic acid, and the C_1 - C_6 alkyl, hydroxy- C_1 - C_6 -alkyl, benzyl, cyclohexyl, and phenyl esters thereof.

8. A process according to claim 1 wherein the weight ratio of said prepolymer to said polyethylenic polymer is 90:10 to 10:90.

9. A composition of matter which is a homogeneous dispersion of chain extended polyurethane and polyethylenic polymer, which composition of matter exhibits a single glass transition temperature.

10. A composition according to claim 9 wherein said prepolymer is the reaction product of a polyol reactant and a polyisocyanate reactant.

11. A composition of matter according to claim 10 wherein said polyol reactant is selected from the group consisting of organic polyols having a molecular weight of 400 to 5,000 and an average OH value of 10 to 1,000.

12. A composition of matter according to claim 10 wherein said polyisocyanate reactant has the formula $Q(NCO)_2$, wherein Q is alkyl containing 4 to 12 carbon atoms, cycloalkyl containing 6 to 15 carbon

atoms, aromatic containing 6 to 15 carbon atoms, or alkylaromatic containing 7 to 15 carbon atoms.

13. A composition of matter according to claim 10 wherein said polyisocyanate reactant is selected from the group consisting of isophorone diisocyanate and methylene bis(isocyanate cyclohexane).

14. A composition of matter according to claim 10 wherein said polyol is selected from the group consisting of dimethylol propionic acid and trimethylol propane.

15. A composition of matter according to claim 9 wherein said polyethylenic polymer is a homopolymer or copolymer of monomers selected from the group consisting of acrylic acid, methacrylic acid, and the C₁-C₆ alkyl, hydroxy-C₁-C₆-alkyl, benzyl, cyclohexyl, and phenyl esters thereof.

16. A composition of matter according to claim 9 wherein the weight ratio of said prepolymer to said polyethylenic polymer is 90:10 to 10:90.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03440

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08L 75/04

US CL : 524/507

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/507

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,927,876 A (COOGAN et al) 22 May 1990 (22-05-90), column 6, lines 9-18.	1-16
Y	US 5,011,881 A (FUJII et al) 30 April 1991 (30-04-91), column 12, line 38.	1-16
Y	US 5,227,422 A (MITSUJI et al) 13 July 1993 (13-07-93), column 22, lines 55-68.	1-16
Y	US 5,541,251 A (BONTINCK et al) 30 July 1996 (30-07-96), column 26, lines 60-68.	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

-	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"G"	document member of the same patent family

Date of the actual completion of the international search

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